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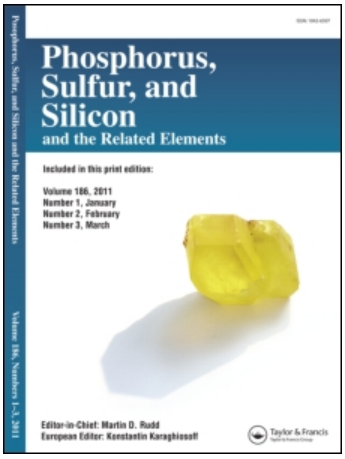

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART VI. THE REACTION OF THE >P—O$^-$ ANIONS WITH BENZYL BROMIDES *para*-SUBSTITUTED IN THE PHENYL RING

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART VI.† THE REACTION OF THE >P—O⁻ ANIONS WITH BENZYL BROMIDES *para*-SUBSTITUTED IN THE PHENYL RING‡

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The reaction of *p*-substituted benzyl bromides with the >P—O⁻ ions in THF, alcohols and toluene as the solvents is described. According to the reduction potential of the *p*-substituted benzyl bromides and the solvent used the formation of the P—C bond, debromination and/or dimerization occur. The principal process is believed to be X-philic substitution, the dimers are formed through a secondary process via SET from the *p*-substituted benzyl anions into the *p*-substituted benzyl bromides.

Key words: Michaelis-Becker reaction, dialkyl phosphites, dialkylphosphinoxides, *p*-substituted benzyl bromides, *p,p'*-substituted bibenzyls, X-philic substitution, SET.

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INTRODUCTION

In the field of phosphorus organic chemistry there are two very important, very famous and very old reactions, namely Michaelis-Becker[1] and Michaelis-Arbuzov[2] reactions. They belong to the most commonly used method for the formation of carbon-phosphorus bonds based on the displacement of a suitable leaving group from the carbon atom by nucleophilic trivalent phosphorus species.

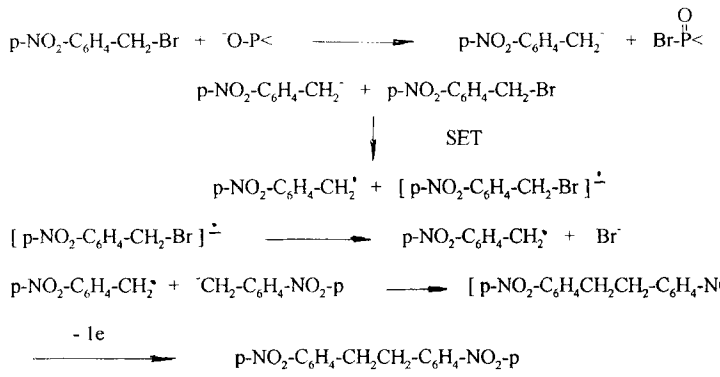
The mechanism of the Michaelis-Becker reaction is often assumed to be the S_N2 process involving the salts of trivalent phosphorus acids.

$$>P—O^- + R — X \rightarrow R — P(O)< + X^-$$

The >P—O⁻ anions give a satisfactory yield of the phosphoryl type products only with primary alkyl halides. Secondary and tertiary alkyl halides give with these anions a poor yield or a complex mixture of the products.

On the other hand dialkyl phosphite anions are known to participate as nucleophiles in aromatic,[3] aliphatic[4] as well as in heteroorganic[5] $S_{RN}1$ processes. G. A. Russell[6] reported that dialkyl phosphite or thiophosphite anions react with *p*-nitrobenzyl chloride, and α,α-dimethyl-*p*-nitrobenzyl chloride to form *p*-nitrobenzylphosphonates. He claimed that this reaction proceeds at least partially by the $S_{RN}1$ scheme involving the >P—O⁻ as well as the >P—S⁻ ions as single electron donors.

†Part V see proceedings of 13th ICPC, Jerusalem 1995.
‡Dedicated to Professor Jan Michalski on the occasion of his 75th birthday.



On the other hand in the literature one can find some examples of an unusual course of the Michaelis-Becker reaction.[7]

We have shown recently[8] that the diisopropyl phosphite anion in the reaction with *p*-nitrobenzyl chloride in THF produces two major products: diisopropyl *p*-nitrobenzylphosphonate and 4,4′-dinitrostilbene; in contrast the treatment of 1 equiv of *p*-nitrobenzyl bromide in THF at 20°C with 1 equiv of the diisopropyl phosphite anion as well as the dibenzylphosphinite anion produces one major product namely: 1,2-di(*p*-nitrophenyl)ethane.

We also studied the reaction of *o*-, *m*- and *p*-nitrobenzyl bromides with sodium dimethyl phosphite as well as sodium diisopropyl phosphite. We discovered that the major product in the reaction of *o*- as well as *p*-nitrobenzyl bromides with the ions of the type >P—O^- is a dimer namely: *o*,*o*′- or *p*,*p*′-dinitrobibenzyl. We believe that the principal process in *o*- and *p*-nitrobenzyl bromide and the >P—O^- anion systems are to be the X-philic substitution, the dimer is formed through a secondary process via SET from the nitrobenzyl anion to nitrobenzyl bromide.[9]

In order to check our postulate of this mechanism as well as to check the scope and limitation of this type of reactivity of the >P—O^- ions, we decided to study other benzyl systems, possessing electron withdrawing groups in the phenyl ring, with different redox potential. In this paper we would like to present the results of this investigation.

RESULTS

We ran the reactions of 1 equiv of *p*-substituted benzyl bromides **1** (*p*-nitro-, *p*-cyano-, *p*-phenylsulfonyl-, *p*-carbethoxy- and *p*-bromo-benzyl bromides) with 1 equiv of $R_2P—O^-$ anion (R = OiPr, CH_2Ph) in THF, iPrOH and toluene. The products distribution strongly depends on the substituent in the *para* position of the phenyl ring, see Table I.

The major product of the reaction of *p*-nitrobenzyl bromide with the >P—O^- ion is dimer **4**, which was showed previously (Table I, run 1–6). In contrast to this the reaction of *p*-cyanobenzyl bromide with the >P—O^- ion is much more complex; we isolated from the reaction mixture: *p*-cyanobenzyl-phosphonate (-phosphin oxide) **2**, dimer **4** (Z = CN) and *p*-cyanotoluene **5** (Table I, run 7–12). We obtained similar

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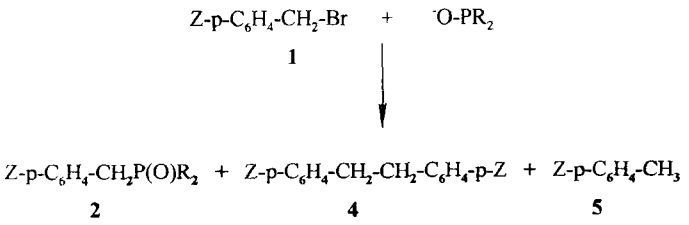

TABLE I

Reaction of the $^{-}O—PR_2$ nucleophile with *p*-substituted benzyl bromides

Run	Z	R	Solvent	% of isolated yield			
				1	2	4	5
1	-NO_2	OiPr	THF	18	-	81	-
2			iPrOH	20	-	79	-
3			$PhCH_3$*	-	-	98	-
4		CH_2Ph	THF	57	-	42	-
5			iPrOH	51	-	48	-
6			$PhCH_3$*	28	-	71	-
7	-CN	OiPr	THF	25	16	34	24
8			iPrOH	42	12	-	44
9			$PhCH_3$*	28	21	17	32
10		CH_2Ph	THF	36	10	26	25
11			iPrOH	42	8	-	48
12			$PhCH_3$*	41	15	12	31
13	-SO_2Ph	OiPr	THF	32	9	28	28
14			iPrOH	48	8	-	42
15			$PhCH_3$*	37	16	14	30
16		CH_2Ph	THF	52	6	12	28
17			iPrOH	47	5	-	46
18			$PhCH_3$*	41	12	9	36
19	-COOEt	OEt	THF	61	24	-	13
20			EtOH	68	21	-	9
21			$PhCH_3$*	62	31	-	5
22		CH_2Ph	THF	57	19	-	23
23			$PhCH_3$*	41	22	-	36
24	-Br	OiPr	THF	28	64	-	7
25			iPrOH	32	60	-	5
26			$PhCH_3$*	11	82	-	5
27		CH_2Ph	THF	25	58	-	16
28			iPrOH	28	57	-	13
29			$PhCH_3$*	17	67	-	14

*Reaction was run at boiling point of the solvent

results in the case of *p*-(phenylsulfonyl)benzyl bromide (Table I, run 13–18). On the other hand the treatment of *p*-carbethoxy- as well as *p*-bromo-benzyl bromides with the >P—O^- ions produces benzylphosphonates **2** (Z = EtO—CO, Br) and toluenes **5** (Z = EtO—CO, Br) (Table I, run 19–29), no dimer **4** was detected.

We also ran the experiments with the >P—O^- ions and *p*-substituted benzyl bro-

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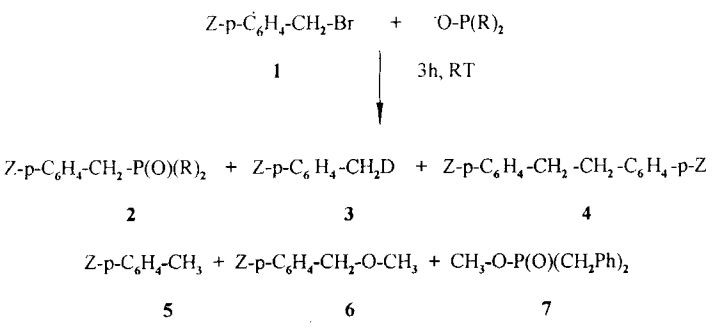

TABLE II

Reaction of the $^{-}O—PR_2$ nucleophile with *p*-substituted benzyl bromides in THF and methanol-O-d

Run	Z	R	solvent	% of isolated yield						
				1	**2**	**3**	**4**	**5**	**6**	**7**
30	NO_2	OCH_3	THF	9	8	-	82	-	-	-
31			CH_3OD	23	3	31	12	-	28	-
4		CH_2Ph	THF	57	-	-	42	-	-	-
32			CH_3OD	23	-	34	11	-	29	38
33	CN	OCH_3	THF	21	27	-	24	27	-	-
34			CH_3OD	29	26	16	-	-	28	-
10		CH_2Ph	THF	36	10	-	26	25	-	-
35			CH_3OD	31	5	44	-	-	19	43
36	SO_2Ph	OCH_3	THF	25	24	-	20	30	-	-
37			CH_3OD	19	22	25	-	-	32	-
16		CH_2Ph	THF	52	6	-	12	28	-	-
38			CH_3OD	26	9	45	-	-	18	32
19	COOEt	OC_2H_5	THF	61	24	-	-	13	-	-
22		CH_2Ph	THF	57	18	-	-	23	-	-
39	COOMe	OCH_3	CH_3OD	45	32	5	-	-	16	-
40		CH_2Ph	CH_3OD	41	17	24	-	-	17	23
41	Br	OCH_3	THF	-	96	-	-	3	-	-
42			CH_3OD	10	55	-	-	-	34	-
27		CH_2Ph	THF	25	58	-	-	16	-	-
43			CH_3OD	13	41	12	-	-	32	10

mides **1** in methanol-O-d. The results of this set of experiments are collected in Table II.

As one can see from this table in all the cases we isolated from the reaction mixture monodeuterated toluene **3**, and ether **6** as a product of the solvolysis process. Dimer **4** was produced only in the reaction carried out in THF in the case of *p*-cyano- and *p*-(phenylsulfonyl)-benzyl bromides used as starting materials. The treatment of *p*-nitrobenzyl bromide with the $>P—O^{-}$ nucleophiles in methanol produces also dimer **4** but with a much lower yield in comparison with the yield obtained in the reaction carried out in THF (see runs 4, 32 and 30, 31, Table II). Another interesting feature is that in the case of dibenzylphosphine oxide applied as a phosphorus nucleophile

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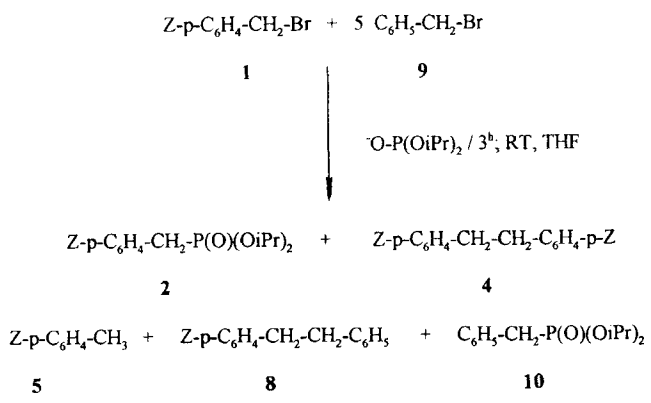

TABLE III

Crossover experiments

Z	% of isolated yield						
	1	2	4	5	8	9	10
NO_2	21	-	78	-	-	97	-
CN	23	13	30	33	-	93	3
SO_2Ph	36	8	26	28	-	94	3

(Table II, runs: 32, 35, 38, 40 and 43) we additionally isolated methyl dibenzylphosphinate **7** from the reaction mixture.

DISCUSSION

Monodeuterated toluene **3** isolated from the reaction mixture of *p*-substituted benzyl bromides **1** and the anion >P—O^-, carried out in methanol-O-d is derived from the initial X-philic substitution product: the *p*-substituted benzyl anion (quenched with methanol-O-d). The isolation of methyl dibenzylphosphinate **7** from the reaction mixture additionally supports our postulate of the X-philic substitution with the >P—O^- anion participation (methyl dibenzylphosphinate is derived in methanol from bromodibenzylphosphinate, which is formed as a result of the X-philic substitution).

The *p*-substituted benzyl anions can *a priori* act as a nucleophilic reagent or single electron donor. We ran the reactions of 1 equiv. of *p*-substituted benzyl bromides **1** (*p*-nitro-, *p*-cyano- and *p*-(phenylsulfonyl)-benzyl bromide), 5 equiv. of benzyl bromide with 1 equiv. of sodium diisopropyl phosphite in THF. From these reaction mixtures we isolated only symmetrical dimer **4** and benzyl bromide **9**. No cross products **8** were detected (Table III).

The results of these crossover experiments strongly suggest that dimer **4** is formed in the SET process rather than in the S_N2 nucleophilic substitution involving the *p*-substituted benzyl anions.

Light can speed up a radical anion substitution process. Numerous instances of light effects have been found, some of them very substantial. In general, it appears

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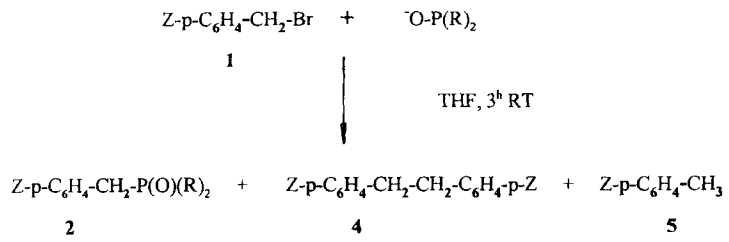

TABLE IV

Light influence on the products distribution of the reaction of *p*-substituted benzyl bromides with the sodium dialkyl phosphite

Z	R	Conditions	% of isolated yield			
			1	2	4	5
NO_2*	OiPr	Darkness	69	-	30	-
		Normal	38	-	61	-
		Light of 500 W bulb	5	-	94	-
CN	OiPr	Darkness	27	15	22	34
		Normal	25	16	34	24
		Light of 500 W bulb	20	11	55	12
SO_2Ph	OiPr	Darkness	40	9	19	31
		Normal	32	9	28	28
		Light of 500 W bulb	29	7	46	16
COOEt	OEt	Normal	61	24	-	13
		Light of 500 W bulb	60	27	-	9
Br	OiPr	Normal	28	64	-	7
		Light of 500 W bulb	29	62	-	8

* Experiments were run for 30 minuts at - 45 °C

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that visible, or near ultraviolet light is effective in promoting these reactions and, indeed, all that is required is illumination by ordinary fluorescent light.[10]

In order to provide evidence for the SET mechanism operating in the reaction in focus we decided to run the reaction for 3 hours in THF at 20°C under a variety of conditions: in darkness, day light and irradiation with 500 W bulb. The results of these experiments are summarized in Table IV.

As one can see from Table IV we found a substantial influence of light on the yield of isolated dimer **4** in the case of *p*-nitro-, *p*-cyano- and *p*-(phenylsulfonyl)-benzyl bromide as a starting material. No dimer was detected in the case of *p*-carbethoxy- and *p*-bromo-benzyl bromides under any of the applied conditions.

We observed the dramatical influence of light on the yield of isolated dimer **4** in the case of *p*-nitrobenzyl bromide (30% in the case of reaction conducted in the darkness vs 94% of the yield in the case of illumination of the reaction flask by 500 W bulb). We also observed substantial influence of light on the yield of dimer **4** in the case of *p*-cyano- as well as *p*-(phenylsulfonyl)-benzyl bromide (22% vs 55% and 19% vs 46%). On the other hand we did not find any light influence on the formation of *p*-substituted benzylphosphonate **2** (*p*-cyano-benzylphosphonate: 15%, 16% and 11% respectively; *p*-(phenylsulfonyl)benzylphosphonate: 9%, 9%, 7% respectively; *p*-carbethoxy-benzylphosphonate: 24%, 27% respectively and *p*-bromo-benzylphosphonate: 64% and 62%).

TABLE V

Selected quantum-chemical parameters of *p*-substituted benzyl bromides: Z—C_6H_4—CH_2—Br

Z	ENERGIES (EV)		CHARGE ON		v/s benzyl bromine CHARGE ON	
	HOMO	LUMO	benzyl carbon	bromine	benzyl carbon	bromine
p-H	-9.56	-0.31	0.1	-0.15	0	0
p-tBu	-9.43	-0.36	0.11	-0.15	0	0
p-Ph	-9.45	-0.37	0.1	-0.15	0	0
p-Br	-9.69	-0.66	0.1	-0.14	-0.01	0.01
p-COOEt	-9.92	-0.72	0.1	-0.14	-0.01	0.01
p-COOMe	-9.93	-0.73	0.09	-0.14	-0.01	0.01
p-CN	-9.93	-1	0.09	-0.14	-0.01	0.02
p-SO_2Ph	-10.21	-1.43	0.09	-0.13	-0.02	0.03
p-NO_2	-10.48	-1.28	0.08	-0.12	-0.02	0.03

All data calculated by AM1, MOPAC'93

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Another interesting feature of this set of experiments is that the yield of *p*-substituted toluene **5** decreases with an increase in the yield of dimer **4**. Again we found a substantial influence of light on the isolated yield of toluene **5** but this time in a reversed order. This last observation further suggests that the *p*-substituted benzyl anions are consumed during the dimers **4** formation; the dimer formation is a secondary process via SET (this reaction is light sensitive) from the *p*-substituted benzyl anions into *p*-substituted benzyl bromides.

As one can see from Tables I and IV in this stage of our research we deal with three different kinds of the *p*-substituted benzyl bromides. *p*-nitrobenzyl bromide belongs to the first category which with the >P—O^- anions forms in THF almost only dimer **4** and in alcohols dimer **4** and toluene **5**. *p*-cyanobenzyl bromide as well as *p*-(phenylsulfonyl)benzyl bromide belong to the second category which with the >P—O^- anions forms preferentially dimer **4**, toluene **5** and some amount of benzylphosphonates **2**. *p*-carbmethoxy-, *p*-carbethoxy- as well as *p*-bromo-benzyl bromide belong to this category which with the >P—O^- anions form phosphoryl type products **2** and some amount of toluene **5**. In this last category of the starting material no dimer formation was observed. The yields of phosphoryl type products **2** depend on the steric effect, the bulky phosphorus nucleophile of the type >P—O^- produces a lower yield of the C—P=O products. Previously[7] we were able to demonstrate that the bulky phosphorus nucleophile of the type >P—O^-, because of the steric hindrance, preferentially attacks the bromine atom in *m*-nitrobenzyl bromide instead of the benzyl carbon atom. Facing the results of our experiments presented in this paper three very important questions arise: 1. What is the major difference between these three categories of the benzyl bromides? 2. How can we explain the different product distributions in the reaction of the >P—O^- nucleophiles with these three categories of starting materials? 3. Can we find a reasonable explanation of the behavior of these three categories of benzyl bromides toward the >P—O^- nucleophiles, which will fit into our proposal of the mechanism of the reaction in focus?

In Table V we collected some quantum-chemical parameters (HOMO, LUMO, charge density) of the selected *p*-substituted benzyl bromides. In Table VI, on the other hand, we collected Hammett σ constants for the substituents applied in this

TABLE VI

Hammett σ constants and reduction potentials of *p*-substituted benzyl bromides

Z	σHammett[#]	$E_{1/2}$ [V] *	$ArCH_2$-Br + -O-P< suggested mechanisms involved
H	0	-1.33	S_NC
tBu	-0.2	-1.22	S_NC
Ph	-0.01	-1.3	S_NC
Br	0.23	-1.13	S_NC , S_NBr
COOEt	0.45	-0.91	S_NC , S_NBr
$PhSO_2$	0.68	-0.75	S_NC , S_NBr / SET
CN	0.66	-0.67	S_NC , S_NBr / SET
NO_2	0.78	-0.4	S_NBr / SET

[#] Chem.Rev. **91**, 165, (1991)
* Helv.Chim..Acta **44**, 1908, (1961) (Hg/ MeOH, MeOLi, SCE)

study and the reduction potentials of the *p*-substituted benzyl bromides. These compounds were selected because all of them have the same general structure. The only way in which these compounds differ from one another is the substituent **Z**, what causes different reactivity toward the >P—O^- nucleophiles.

As we demonstrated previously,[8] benzyl bromide, *p*-tBu-benzyl bromide as well as *p*-phenyl-benzyl bromide produce with the >P—O^- anions the Michaelis-Becker product **2** (compounds with the C—P=O moiety) only. The results of our study show that *p*-bromo-, *p*-carbmethoxy- as well as *p*-carbethoxy-benzyl bromides produce with the >P—O^- nucleophiles phosphonates **2** and toluenes **5**. In the case of *p*-cyano- and *p*-(phenylsulfonyl)-benzyl bromide we isolated three major products from the reaction mixture with the >P—O^- reagents, namely phosphonates **2**, dimer **4** and toluenes **5**. In contrast from the reaction mixture of *p*-nitrobenzyl bromide and the >P—O^- nucleophiles in THF we isolated one major product, namely *p,p'*-dinitrobibenzyl **4**.

The examination of Table V shows that from the theoretical calculation it appears that the highest electron density on the bromine atom is in the case of benzyl bromide and the lowest one in the case of *p*-nitrobenzyl bromide. This observation would explain the X-philic substitution (at least partially) in the case of *p*-substituted benzyl bromides possessing substituents with positive values of Hammett σ constants.

Taking into consideration the isolation of toluene **5** and methyl dibenzylphosphinate **7** from the reaction mixture as well as the charge distribution presented in Table V one can conclude that the nucleophilic displacement on the bromine with the release of the *p*-substituted benzyl anion is the first step in the reaction under investigation. The initially formed *p*-substituted benzyl anion in the carried out reaction can act as a single electron donor (if a suitable acceptor in the reaction mixture is present) to yield dimer **4** as a final product or can act as a base (the proton transfer reaction) to yield *p*-substituted toluene **5** as a final product.

The data collected in Table VI suggest the following order of electron acceptor ability for families of the *p*-substituted benzyl bromides applied in our study: *p*-nitro- > *p*-cyano- > *p*-(phenylsulfonyl)- > *p*-carbethoxy- > *p*-bromo- > *p*-tBu- > *p*-phenyl- > benzyl bromide. It is well known that the success of the electron transfer reaction is the result of a less negative reduction potential of the alkyl, aryl halides.[11] This

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less negative reduction potential can be caused by the presence of an electron-withdrawing group in the molecule. Benzyl bromides activated by electron-withdrawing substituents in the para position (NO_2; CN; $PhSO_2$) possess a fairly high oxidizing power (see Table VI) and it should not be surprising to see electron transfer reactions with these *p*-substituted benzyl anions.

Because of the less negative reduction potential of *p*-nitrobenzyl bromide in the presented family, the electron transfer reaction is a very fast process and its result is the dimer **4** formation in a very high yield. On the other hand the reduction potentials for *p*-cyanobenzyl bromide and *p*-(phenylsulfonyl)benzyl bromide are -0.67 V and -0.75 V respectively. It means that the electron acceptor ability of these compounds is much lower than of *p*-nitrobenzyl bromide. In consequence the reaction rate for an electron transfer of the above mentioned systems is relatively smaller than for the system of *p*-nitrobenzyl bromide/*p*-nitrobenzyl anion, thus the proton transfer would be an important competing process. This is precisely what was observed. This category of the starting material produces in the reaction with the >P—O^- nucleophiles dimer **4** (via SET) and toluenes **5** (via proton transfer). In contrast *p*-carbethoxybenzyl bromide as well as *p*-bromobenzylbromide possess a very negative reduction potential, the acceptor ability of these structures is very low and probably they are not able to participate in the electron transfer reaction with the *p*-bromo- as well as *p*-carbethoxy-benzyl anions or they undergo the electron transfer reaction at a very slow rate. The competition process, namely the proton transfer has much bigger reaction rate than the electron transfer, which would largely result in the formation of toluene **5** as a main product. Additionally, what should be pointed out, in the reaction between *p*-bromobenzyl bromide as well as *p*-carbalkoxybenzyl bromides and the >P—O^- nucleophiles a substantial amount of phosphonates **2** (good proton donors) is produced (Table I runs 19 to 29 and Table II runs 19 to 43). The presence of phosphonates **2** in the reaction mixture will additionally favour the proton transfer reaction, which actually we observed in our study.

In conclusion we can say that the isolated products from the reaction mixture of the >P—O^- nucleophiles with *p*-substituted benzyl bromides (possessing substituents with a positive value of Hammett σ constants), were toluene **5**, methyl dibenzylphosphinate **7** and bibenzyl **4**; the influence of light on the product distributions as well as the presented correlation between the reduction potentials of *p*-substituted benzyl bromides and the reaction course strongly support our proposal (the X-philic substitution and the following electron transfer process) of the mechanism of the reaction in focus.

Additional work is under way to proof the presence of *p*-nitrobenzyl radicals in the reaction mixture and to determine whether the dimer formation is a chain process or the nonchain radical dimerization. This work is in progress and the results will be published successively.

EXPERIMENTAL

Dialkyl phosphites were purchased from Aldrich and distilled before use. Sodium hydride (Aldrich) was washed with hexane to remove paraffin oil. Tetrahydrofuran or toluene was dried with sodium-potassium alloy. Isopropanol was dried with calcium hydride. Melting points were uncorrected. Mass spectra (FD) were recorded on an AMD Intectra 604 apparatus. IR spectra were taken on a Jena-Zeiss IR 10 apparatus. ^{31}PNMR and ^{1}HNMR spectra were recorded with a Varian apparatus at 60, 200 or 500 MHz. 4-Phen-

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ylbenzyl bromide,[12] 4-bromobenzyl bromide,[13] 4-carbethoxybenzyl bromide,[14] 4-carbmethoxybenzyl bromide,[15] 4-(phenylsulfonyl)benzyl bromide,[16] were prepared by known methods. All other 4-substituted benzyl bromides were purchased from Aldrich. The half-wave potentials listed in Table VI which were not obtained by Klopman[23] were calculated[24] and related to MeOH solution. HOMO, LUMO energies and partial charges were calculated by means of semiempirical AM1 method contained in MOPAC 93.[25]

The Michaelis-Becker Reaction Between 4-Substituted Benzyl Bromide **1** *and the Sodium Salt of Diisopropyl Phosphite as well as Dibenzylphosphine Oxide: General Procedure*

A. In THF Solution

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF was added diisopropyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 10 mL of THF. When the evolution of hydrogen had ceased, 4-substituted benzyl bromide **1** (4-nitrobenzyl bromide, 4-cyanobenzyl bromide, 4-(phenylsulfonyl)benzyl bromide, 4-carbethoxybenzyl bromide, 4-bromobenzyl bromide) (2.5 mmol) in 5 mL of THF were added and the reaction mixture was stirred for 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography. The yields are shown in Table I.

Run 1

4-nitrobenzyl bromide **1a** (eluted with hexane) 0.097 g (18%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.276 g (81%)
m.p. 180–182°C (lit. 178–181°C).[17]
^{1}HNMR ($CDCl_3$) δ = 2.90 (s, CH_2, 4H), 6.83 (d, J = 8.00 Hz, aromat, 4H), 7.66 (d, J = 8.00 Hz, aromat, 4H)

Run 4

4-nitrobenzyl bromide **1a** (eluted with hexane) 0.308 g (57%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.143 g (42%)

Run 7

4-cyanotoluene **5b** (eluted with hexane:chloroform 9:1) 0.070 g (24%)
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 4:1) 0.124 g (25%)
1,2-di(*p*-cyanophenyl)ethane **4b** (eluted with chloroform) 0.098 g (34%)
m.p. 197–198°C (lit. 198°C).[18]
IR (KBr) ν = 2250 CN cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.93 (s, CH_2, 4H), 7.10 (d, J = 8.00 Hz, aromat, 4H), 7.46 (d, J = 8.00 Hz, aromat, 4H)
diisopropyl (4-cyanophenyl)methylphosphonate **2b** (eluted with chloroform) 0.045 g (16%)
IR (Film) ν = 1265 P=O, 1020 P—O—C, 2250 CN cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 1.19 (d, J = 6.23 Hz, CH_3, 6H), 1.29 (d, J = 6.23 Hz, CH_3, 6H) 3.17 (d, J = 22.34 Hz, CH_2P, 2H), 4.50–4.70 (m, P—O—CH<, 2H), 7.37–7.50 (m, aromat, 2H), 7.61 (d, J = 8.06 Hz, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 22.90
Acid hydrolysis of this material yielded (4-carboxyphenyl)methylphosphonic acid m.p. 334–335°C (lit. 335°C).[19]

Run 10

4-cyanotoluene **5b** (eluted with hexane:chloroform 9:1) 0.074 g (25%)
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 4:1) 0.176 g (36%)
1,2-di(*p*-cyanophenyl)ethane **4b** (eluted with chloroform) 0.075 g (26%)
(4-cyanophenyl)methyldibenzylphosphine oxide **2c** (eluted with chloroform) 0.086 g (10%) m.p. 175–177°C
IR (KBr) ν = 1200 P=O, 2250 CN cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.04 (d, J = 13.47 Hz, CH_2P, 6H), 7.00–7.60 (m, aromat, 14H)
^{31}PNMR ($CDCl_3$) δ = 40.27
Anal. Calcd. for $C_{22}H_{20}NOP$: C, 76.50; H, 5.84; found: C, 76.36; H, 5.72

Run 13

(4-methylphenyl)phenyl sulfon **5d** (eluted with hexane:chloroform 2:1) 0.165 g (28%)
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform) 0.252 g (32%)
1,2-di(4-(phenylsulfonyl)phenyl)ethane **4d** (eluted with hexane:chloroform 2:3) 0.162 g (28%)

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m.p. 251–252°C
IR (KBr) ν = 1320, 1175 SO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.96 (s, CH_2, 4H), 7.24–7.32 (m, aromat, 4H), 7.48–7.64 (m, aromat, 6H), 7.84–8.00 (m, aromat, 8H)
Anal. Calcd. for $C_{26}H_{22}O_4S_2$: C, 67.50; H, 4.80; found: C, 67.42; H, 4.61
diisopropyl (4-(phenylsulfonyl)phenyl)methylphosphonate **2d** (eluted with chloroform) 0.087 g (9%)
m.p. 91–93°C
IR (KBr) ν = 1260 P=O, 1015 P—O—C, 1320, 1175 SO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 1.14 (d, J = 5.90 Hz, CH_3, 6H), 1.28 (d, J = 5.90 Hz, CH_3, 6H) 3.15 (d, J = 22.00 Hz, CH_2P, 2H), 4.55–4.65 (m, P—O—CH<, 2H), 7.42–7.60 (m, aromat, 5H), 7.86–7.98 (m, aromat, 4H)
^{31}PNMR ($CDCl_3$) δ = 23.10
Anal. Calcd. for $C_{19}H_{25}O_5PS$: C, 57.56; H, 6.36; found: C, 57.38; H, 6.42

Run 16

(4-methylphenyl)phenyl sulfon **5d** (eluted with hexane:chloroform 2:1) 0.163 g (28%)
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform 1:1) 0.406 g (52%)
1,2-di(4-(phenylsulfonyl)phenyl)ethane **4d** (eluted with hexane:chloroform 2:3) 0.069 g (12%)
(4-(phenylsulfonyl)phenyl)methylidibenzylphosphine oxide **2e** (eluted with chloroform) 0.069 g (6%)
m.p. 154–156°C
IR (KBr) ν = 1190 P=O, 1320, 1175 SO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.04 (d, J = 13.57 Hz, CH_2P, 6H), 7.10–8.00 (m, aromat, 19H)
^{31}PNMR ($CDCl_3$) δ = 41.81
Anal. Calcd. for $C_{27}H_{25}O_3PS$: C, 70.42; H, 5.47; found: C, 70.51; H, 5.33

Run 19

4-carbethoxytoluene **5f** (eluted with hexane:ether 4:1) 0.054 g (13%)
4-carbethoxybenzyl bromide **1f** (eluted with hexane:ether 2:1) 0.370 g (61%)
diethyl (4-carbethoxypenyl)methylphosphonate **2f** (eluted with chloroform) 0.180 g (24%)
IR (Film) ν = 1270 P=O, 1055 P—O—C, 1705 C=O, 1290 C—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 1.25 (t, J = 7.00 Hz, P—O—C—CH_3, 6H), 1.39 (t, J = 7.08 Hz, COOC—CH_3, 3H), 3.23 (d, J = 22.33 Hz, PCH_2, 2H), 3.90–4.20 (m, P—O—CH_2—C, 4H), 4.37 (q, J = 7.15 Hz, $COOCH_2$—C, 2H), 7.30–7.45 (m, aromat, 2H), 7.99 (d, J = 8.06 Hz, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 25.84

Run 22

4-carbethoxytoluene **5f** (eluted with hexane:ether 4:1) 0.094 g (23%)
4-carbethoxybenzyl bromide **1f** (eluted with hexane:ether 2:1) 0.348 g (57%)
(4-carbethoxyphenyl)methyldibenzylphosphine oxide **2g** (eluted with chloroform) 0.188 g (19%)
m.p. 148–150°C
IR (KBr) ν = 1200 P=O, 1700 C=O, 1300 C—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 1.23 (t, J = 7.00 Hz, CH_3, 3H), 2.86 (d, J = 13.00 Hz, CH_2P, 6H), 4.06 (q, J = 7.00 Hz, O—H_2, 2H), 6.90–7.70 (m, aromat, 14H)
^{31}PNMR ($CDCl_3$) δ = 41.32
Anal. Calcd. for $C_{24}H_{25}O_3P$: C, 73.45; H, 6.42; found: C, 73.60; H, 6.38

Run 24

4-bromotoluene **5h** (eluted with hexane) 0.031 g (7%)
4-bromobenzyl bromide **1h** (eluted with hexane:chloroform 4:1) 0.177 g (28%)
diisopropyl (4-bromophenyl)methylphosphonate **2h** (eluted with chloroform) 0.533 g (64%)
IR (Film) ν = 1265 P=O, 1030 P—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.03 (d, J = 21.71 Hz, CH_2P, 2H), 1.16 (d, J = 6.21 Hz, CH_3, 6H), 1.26 (d, J = 6.21 Hz, CH_3, 6H), 4.45–4.70 (m, O—CH<, 2H), 7.10–7.25 (m, aromat, 2H), 7.33–7.44 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 24.05
The product was identified by comparison of the IR and NMR spectra with an authentic sample.[20]

Run 27

4-bromotoluene **5h** (eluted with hexane) 0.070 g (16%)
4-bromobenzyl bromide **1h** (eluted with hexane:chloroform 4:1) 0.155 g (25%)
(4-bromophenyl)methyldibenzylphosphine oxide **2i** (eluted with chloroform) 0.579 g (58%) m.p. 160–161°C

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IR (KBr) ν = 1195 P=O cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.04 (d, J = 13.88 Hz, CH_2P, 6H), 7.05–7.48 (m, aromat, 14H)
^{31}PNMR ($CDCl_3$) δ = 40.73
Anal. Calcd. for $C_{21}H_{20}BrOP$: C, 63.17; H, 5.05; found: C, 62.94; H, 5.16

B. In Isopropanol Solution

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of iPrOH and to the resultant mixture diisopropyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 10 mL of iPrOH and 4-substituted benzyl bromide **1** (4-nitrobenzyl bromide, 4-cyanobenzyl bromide, 4-(phenylsulfonyl)benzyl bromide, 4-carbethoxybenzyl bromide, 4-bromobenzyl bromide) (2.5 mmol) in 5 mL of THF were added. The reaction mixture was stirred for 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography. The products were identified by comparison of the IR and NMR spectra with those of authentic samples. The yields are shown in Table I.

Run 2

4-nitrobenzyl bromide **1a** (eluted with hexane) 0.108 g (20%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.269 g (79%)

Run 5

4-nitrobenzyl bromide **1a** (eluted with hexane) 0.274 g (51%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.163 g (48%)

Run 8

4-cyanotoluene **5b** (eluted with hexane:chloroform 9:1) 0.129 g (44%)
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 4:1) 0.026 g (42%)
diisopropyl (4-cyanophenyl)methylphosphonate **2b** (eluted with chloroform) 0.085 g (12%)

Run 11

4-cyanotoluene **5b** (eluted with hexane:chloroform 9:1) 0.141 g (48%)
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 4:1) 0.206 g (42%)
(4-cyanophenyl)methyldibenzylphosphine oxide **2c** (eluted with chloroform) 0.069 g (8%)

Run 14

(4-methylphenyl)phenyl sulfon **5d** (eluted with hexane:chloroform 2:1) 0.244 g (42%)
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform) 0.373 g (48%)
diisopropyl (4-(phenylsulfonyl)phenyl)methylphosphonate **2d** (eluted with chloroform) 0.079 g (8%)

Run 17

(4-methylphenyl)phenyl sulfon **5d** (eluted with hexane:chloroform 2:1) 0.267 g (46%)
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform 1:1) 0.364 g (47%)
(4-(phenylsulfonyl)phenyl)methyldibenzylphosphine oxide **2e** (eluted with chloroform) 0.060 g (5%)

Run 20 (In Ethanol Solution)

4-carbethoxytoluene **5f** (eluted with hexane:ether 4:1) 0.038 g (9%)
4-carbethoxybenzyl bromide **1f** (eluted with hexane:ether 2:1) 0.413 g (68%)
diethyl (4-carbethoxyphenyl)methylphosphonate **2f** (eluted with chloroform) 0.159 g (21%)

Run 25

4-bromotoluene **5h** (eluted with hexane) 0.022 g (5%)
4-bromobenzyl bromide **1h** (eluted with hexane:chloroform 4:1) 0.200 g (32%)
diisopropyl (4-bromophenyl)methylphosphonate **2h** (eluted with chloroform) 0.503 g (60%)

Run 28

4-bromotoluene **5h** (eluted with hexane) 0.056 g (13%)
4-bromobenzyl bromide **1h** (eluted with hexane:chloroform 4:1) 0.175 g (28%)
(4-bromophenyl)methyldibenzylphosphine oxide **2i** (eluted with chloroform) 0.567 g (57%)

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C. In Toluene Solution

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of toluene was added diisopropyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 5 mL of toluene. When the evolution of hydrogen had ceased, 4-substituted benzyl bromide **1** (4-nitrobenzyl bromide, 4-cyanobenzyl bromide, 4-(phenylsulfonyl)benzyl bromide, 4-carbethoxybenzyl bromide, 4-bromobenzyl bromide) (2.5 mmol) in 10 mL of toluene were added and the reaction mixture was stirred for 3 hours at boiling point of the solvent, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography. The products were identified by comparison of the IR and NMR spectra with those of authentic samples. The yields are shown in Table I.

Run 3

1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.332 g (98%)

Run 6

4-nitrobenzyl bromide **1a** (eluted with hexane) 0.151 g (28%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.242 g (71%)

Run 9

4-cyanotoluene **5b** (eluted with hexane:chloroform 9:1) 0.094 g (32%)
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 4:1) 0.137 g (28%)
1,2-di(*p*-cyanophenyl)ethane **4b** (eluted with chloroform) 0.051 g (17%)
diisopropyl (4-cyanophenyl)methylphosphonate **2b** (eluted with chloroform) 0.147 g (21%)

Run 12

4-cyanotoluene **5b** (eluted with hexane:chloroform 9:1) 0.091 g (31%)
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 4:1) 0.202 g (41%)
1,2-di(*p*-cyanophenyl)ethane **4b** (eluted with chloroform) 0.035 g (12%)
(4-cyanophenyl)methyldibenzylphosphine oxide **2c** (eluted with chloroform) 0.131 g (15%)

Run 15

(4-methylphenyl)phenyl sulfon **5d** (eluted with hexane:chloroform 2:1) 0.174 g (30%)
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform) 0.288 g (37%)
1,2-di(4-(phenylsulfonyl)phenyl)ethane **4d** (eluted with hexane:chloroform 2:3) 0.081 g (14%)
diisopropyl (4-(phenylsulfonyl)phenyl)methylphosphonate **2d** (eluted with chloroform) 0.159 g (16%)

Run 18

(4-methylphenyl)phenyl sulfon **5d** (eluted with hexane:chloroform 2:1) 0.209 g (36%)
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform 1:1) 0.319 g (41%)
1,2-di(4-(phenylsulfonyl)phenyl)ethane **4d** (eluted with hexane:chloroform 2:3) 0.052 g (9%)
(4-(phenylsulfonyl)phenyl)methyldibenzylphosphine oxide **2e** (eluted with chloroform) 0.138 g (12%)

Run 21

4-carbethoxytoluene **5f** (eluted with hexane:ether 4:1) 0.021 g (5%)
4-carbethoxybenzyl bromide **1f** (eluted with hexane:ether 2:1) 0.377 g (62%)
diethyl (4-carbethoxyphenyl)methylphosphonate **2f** (eluted with chloroform) 0.233 g (31%)

Run 23

4-carbethoxytoluene **5f** (eluted with hexane:ether 4:1) 0.148 g (36%)
4-carbethoxybenzyl bromide **1f** (eluted with hexane:ether 2:1) 0.249 g (41%)
(4-carbethoxyphenyl)methyldibenzylphosphine oxide **2g** (eluted with chloroform) 0.216 g (22%)

Run 26

4-bromotoluene **5h** (eluted with hexane) 0.021 g (5%)
4-bromobenzyl bromide **1h** (eluted with hexane:chloroform 4:1) 0.069 g (11%)
diisopropyl (4-bromophenyl)methylphosphonate **2h** (eluted with chloroform) 0.687 g (82%)

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Run 29

4-bromotoluene **5h** (eluted with hexane) 0.060 g (14%)
4-bromobenzyl bromide **1h** (eluted with hexane:chloroform 4:1) 0.106 g (17%)
(4-bromophenyl)methyldibenzylphosphine oxide **2i** (eluted with chloroform) 0.669 g (67%)

Reaction of 4-Substituted Benzyl Bromide **1** *with Dimethyl Phosphite in THF Solution: General Procedure*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF was added dimethyl phosphite (2.5 mmol, 0.275 g, 0.23 mL) in 10 mL of THF. When the evolution of hydrogen had ceased, 4-substituted benzyl bromide **1** (4-nitrobenzyl bromide, 4-cyanobenzyl bromide, 4-(phenylsulfonyl)benzyl bromide, 4-bromobenzyl bromide) (2.5 mmol) in 5 mL of THF were added and the reaction mixture was stirred for 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography. The yields are shown in Table II.

Run 30

4-nitrobenzyl bromide **1a** (eluted with hexane) 0.049 g (9%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.280 g (82%)
dimethyl (4-nitrophenyl)methylphosphonate **2a** (eluted with chloroform) 0.049 g (8%)
m.p. 74–75°C (lit. 75°C).[21]
IR (KBr) ν = 1260 P=O, 1040 P—O—C, 1530, 1350 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.28 (d, J = 22.42 Hz, CH_2P, 2H), 3.71 (d, J = 10.92 Hz, $POCH_3$, 6H), 7.08–7.18 (m, aromat, 2H), 7.75–7.85 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 27.24

Run 33

4-cyanotoluene **5b** (eluted with hexane:chloroform 9:1) 0.079 g (27%)
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 4:1) 0.109 g (21%)
1,2-di(*p*-cyanophenyl)ethane **4b** (eluted with chloroform) 0.070 g (24%)
dimethyl (4-cyanophenyl)methylphosphonate **2j** (eluted with chloroform) 0.152 g (27%)
m.p. 75–76°C
IR (KBr) ν = 1265 P=O, 1050 P—O—C, 2250 CN cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.21 (d, J = 22.34 Hz, CH_2P, 2H), 3.69 (d, J = 10.91 Hz, $POCH_3$, 6H), 7.36–7.46 (m, aromat, 2H), 7.61 (d, J = 7.98 Hz, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 27.53

Acid hydrolysis of this material yielded (4-carboxyphenyl)methylphosphonic acid m.p. 334–335°C (lit. 335°C).[19]

Run 36

(4-methylphenyl)phenyl sulfon **5d** (eluted with hexane:chloroform 2:1) 0.174 g (30%)
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform 1:1) 0.194 g (25%)
1,2-di(4-(phenylsulfonyl)phenyl)ethane **4d** (eluted with hexane:chloroform 2:3) 0.116 g (20%)
dimethyl (4-(phenylsulfonyl)phenyl)methylphosphonate **2m** (eluted with chloroform) 0.213 g (24%)
m.p. 117–118°C
IR (KBr) ν = 1260 P=O, 1050 P—O—C, 1320, 1175 SO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.21 (d, J = 22.26 Hz, CH_2P, 2H), 3.67 (d, J = 10.94 Hz, $POCH_3$, 6H), 7.40–7.65 (m, aromat, 5H), 7.85–8.00 (m, aromat, 4H)
^{31}PNMR ($CDCl_3$) δ = 27.66
Anal. Calcd. for $C_{15}H_{17}O_5PS$: C, 52.93; H, 5.04; found: C, 52.61; H, 5.12

Run 41

4-bromotoluene **5h** (eluted with hexane) 0.012 g (3%)
dimethyl (4-bromophenyl)methylphosphonate **2s** (eluted with chloroform) 0.673 g (96%)
m.p. 49–51°C
IR (KBr) ν = 1260 P=O, 1050 P—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.11 (d, J = 21.61 Hz, CH_2P, 2H), 3.68 (d, J = 10.91 Hz, $POCH_3$, 6H), 7.10–7.25 (m, aromat, 2H), 7.37–7.50 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 28.49

The product was identified by comparison of the IR and NMR spectra with an authentic sample.[20]

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Reaction of 4-Substituted Benzyl Bromide **1** *with Dimethyl Phosphite or Dibenzylphosphine Oxide in the Presence of NaOCH, in Methanol-O-d: General Procedure*

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of methanol-O-d and into the resultant mixture dimethyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 5 mL of methanol-O-d and 4-substituted benzyl bromide **1** (4-nitrobenzyl bromide, 4-cyanobenzyl bromide, 4-(phenylsulfonyl)benzyl bromide, 4-carbmethoxybenzyl bromide, 4-bromobenzyl bromide) (2.5 mmol) in 10 mL of methanol-O-d were added. The reaction mixture was stirred for 3 hours at room temperature, then diluted with 75 mL of ether, washed with 50 ml NH_4Cl saturated solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography. The yields are shown in Table II.

Run 31

4-methyl-*d*-nitrobenzene **3a** (eluted with hexane:chloroform 9:1) 0.108 g (31%)
m.p. 53–55°C
IR (KBr) ν = 1520, 1355 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.45 (t, J = 2.24 Hz, CH_2D, 2H), 7.26–7.36 (m, aromat, 2H), 8.06–8.16 (m, aromat, 2H)
Deuterium incorporation minimum value 96%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-nitrobenzyl bromide **1a** (eluted with hexane:chloroform 9:1) 0.123 g (23%)
4-nitrobenzyl methyl ether **6a** (eluted with hexane:chloroform 2:1) 0.117 g (28%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.041 g (12%)
dimethyl (4-nitrophenyl)methyl-d_2-phosphonate **2w** (eluted with chloroform) 0.020 g (3%) m.p. 74–75°C
IR (KBr) ν = 1260 P═O, 1040 P—O—C, 1530, 1350 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.73 (d, J = 10.92 Hz, $POCH_3$, 6H), 7.08–7.18 (m, aromat, 2H), 7.75–7.85 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 27.31

Run 32

4-methyl-*d*-nitrobenzene **3a** (eluted with hexane:chloroform 9:1) 0.117 g (34%)
Deuterium incorporation minimum value 96%, determined by using mass spectroscopic analysis and ^{1}HNMR.
4-nitrobenzyl bromide **1a** (eluted with hexane:chloroform 9:1) 0.124 g (23%)
4-nitrobenzyl methyl ether **6a** (eluted with hexane:chloroform 2:1) 0.121 g (29%)
1,2-di(*p*-nitrophenyl)ethane **4a** (eluted with chloroform) 0.037 g (11%)
methyl dibenzylphosphinate **7** (eluted with chloroform) 0.247 g (38%)
m.p. 63–65°C, (lit. 75°C).[22]
IR (KBr) ν = 1230 P═O, 1065 P—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.08 (d, J = 16.28 Hz, CH_2P, 4H), 3.57 (d, J = 10.50 Hz, P—O—CH_3, 3H), 7.20–7.40 (m, C_6H_5, 10H)
^{31}PNMR ($CDCl_3$) δ = 49.80

Run 34

4-methyl-*d*-benzonitril **3b** (eluted with hexane:chloroform 9:1) 0.047 g (16%)
m.p. 27–28°C
IR (KBr) ν = 2250 CN cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.41 (t, J = 2.30 Hz, CH_2D, 2H), 7.23–7.32 (m, aromat, 2H), 7.51–7.59 (m, aromat, 2H)
Deuterium incorporation minimum value 98%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 9:1) 0.142 g (29%)
4-cyanobenzyl methyl ether **6b** (eluted with hexane:chloroform 2:1) 0.103 g (28%)
IR (Film) ν = 2250 CN, 1120 C—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.42 (s, O—CH_3, 3H), 4.51 (s, CH_2—O, 2H), 7.44 (d, J = 8.34 Hz, aromat, 2H), 7.64 (d, J = 8.39 Hz, aromat, 2H)
dimethyl (4-cyanophenyl)methyl-d_2-phosphonate **2k** (eluted with chloroform) 0.148 g (26%)
m.p. 74–76°C
IR (KBr) ν = 1260 P═O, 1050 P—O—C, 2250 CN cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.68 (d, J = 10.91 Hz, P—O—CH_3, 6H), 7.35–7.45 (m, aromat, 2H), 7.60 (d, J = 7.83 Hz, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 27.59

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Acid hydrolysis of this material yielded a (4-carboxyphenyl)methylphosphonic acid m.p. 334–335°C (lit. 335°C).[19]

Run 35

4-methyl-*d*-benzonitril **3b** (eluted with hexane:chloroform 9:1) 0.130 g (44%)
Deuterium incorporation minimum value 98%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-cyanobenzyl bromide **1b** (eluted with hexane:chloroform 9:1) 0.152 g (31%)
4-cyanobenzyl methyl ether **6b** (eluted with hexane:chloroform 2:1) 0.070 g (19%)
methyl dibenzylphosphinate **7** (eluted with chloroform) 0.280 g (43%)
(4-cyanophenyl)methyl-d_2-dibenzylphosphine oxide **2l** (eluted with chloroform) 0.043 g (5%)
m.p. 175–178°C
IR (KBr) ν = 1200 P=O, 2250 CN cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.04 (d, J = 13.47 Hz, CH_2P, 4H), 7.00–7.60 (m, aromat, 14H)
^{31}PNMR ($CDCl_3$) δ = 40.32
Anal. Calcd. for $C_{22}H_{18}D_2NOP$: C, 76.06; HD, 6.38; found: C, 76.25; HD, 6.07

Run 37

(4-methyl-*d*-phenyl)phenyl sulfon **3d** (eluted with hexane:chloroform 4:1) 0.146 g (25%)
m.p. 125–127°C
IR (KBr) ν = 1320, 1175 SO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.36 (t, J = 2.22 Hz, CH_2D, 2H), 7.20–7.35 (m, aromat, 2H), 7.35–7.65 (m, aromat, 3H), 7.70–8.00 (m, aromat, 4H)
Deuterium incorporation minimum value 97%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform 2:1) 0.148 g (19%)
(4-(phenylsulfonyl)phenyl)methyl methyl ether **6d** (eluted with hexane:chloroform 1:1) 0.210 g (32%)
m.p. 92–93°C
IR (KBr) ν = 1310, 1170 SO_2, 1120 C—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.40 (s, OCH_3, 3H), 4.49 (s, CH_2O, 2H), 7.41–7.62 (m, aromat, 5H), 7.87–7.99 (m, aromat, 4H)
dimethyl (4-(phenylsulfonyl)phenyl)methyl-d_2-phosphonate **2n** (eluted with chloroform) 0.188 g (22%)
m.p. 117–119°C
IR (KBr) ν = 1260 P=O, 1050 P—O—C, 1320, 1175 SO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.67 (d, J = 10.95 Hz, $POCH_3$, 6H), 7.40–7.65 (m, aromat, 5H), 7.85–8.00 (m, aromat, 4H)
^{31}PNMR ($CDCl_3$) δ = 27.68

Run 38

(4-methyl-*d*-phenyl)phenyl sulfon **3d** (eluted with hexane:chloroform 4:1) 0.262 g (45%)
Deuterium incorporation minimum value 97%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-(phenylsulfonyl)benzyl bromide **1d** (eluted with hexane:chloroform 2:1) 0.202 g (26%)
(4-(phenylsulfonyl)phenyl)methyl methyl ether **6d** (eluted with hexane:chloroform 1:1) 0.118 g (18%)
methyl dibenzylphosphinate **7** (eluted with chloroform) 0.208 g (32%)
Spectral data were identified with those of an authentical sample.
(4-(phenylsulfonyl)phenyl)methyl-d_2-dibenzylphosphine oxide **2o** (eluted with chloroform) 0.104 g (9%)
m.p. 154–157°C
IR (KBr) ν = 1200 P=O, 1320, 1175 SO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.04 (d, J = 13.57 Hz, CH_2P, 4H), 7.10–8.00 (m, aromat, 19H)
^{31}PNMR ($CDCl_3$) δ = 41.73
Anal. Calcd. for $C_{27}H_{23}D_2O_3PS$: C, 70.11; HD, 5.88; found: C, 70.32; HD, 5.57

Run 39

methyl 4-methyl-*d*-benzoate **3p** (eluted with hexane:ether 4:1) 0.019 g (5%)
IR (Film) ν = 1710 C=O, 1295 C—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.37 (t, J = 2.30 Hz, CH_2D, 2H), 3.88 (s, $COOCH_3$, 3H), 7.18–7.24 (m, aromat, 2H), 7.84–7.89 (m, aromat, 2H)
Deuterium incorporation minimum value 99%, determined by using mass spectroscopic analysis and ^{1}HNMR.
4-carbmethoxybenzyl bromide **1p** (eluted with hexane:ether 4:1) 0.258 g (45%)

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4-carbmethoxybenzyl methyl ether **6p** (eluted with hexane:ether 2:1) 0.072 g (16%)
IR (Film) ν = 1710 C=O, 1290 C(O)OC, 1125 C—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.40 (s, OCH_3, 3H), 3.90 (s, $COOCH_3$, 3H), 4.50 (s, CH_2O, 2H), 7.34–7.46 (m, aromat, 2H), 7.96–8.08 (m, aromat, 2H)
dimethyl (4-carbmethoxyphenyl)methyl-d_2-phosphonate **2p** (eluted with chloroform) 0.208 g (32%)
IR (Film) ν = 1260 P=O, 1050 P—O—C, 1710 C=O, 1295 C(O)OC cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.66 (d, J = 10.91 Hz, $POCH_3$, 6H), 3.89 (s, $COOCH_3$, 3H), 7.30–7.40 (m, aromat, 2H), 7.90–8.00 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 28.30

Acid hydrolysis of this material yielded (4-carboxyphenyl)methylphosphonic acid m.p. 334–335°C (lit. 335°C).[19]

Run 40

methyl 4-methyl-*d*-benzoate **3p** (eluted with hexane:ether 4:1) 0.091 g (24%)
Deuterium incorporation minimum value 99%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-carbmethoxybenzyl bromide **1p** (eluted with hexane:ether 4:1) 0.235 g (41%)
4-carbmethoxybenzyl methyl ether **6p** (eluted with hexane:ether 2:1) 0.077 g (17%)
methyl dibenzylphosphinate **7** (eluted with chloroform) 0.150 g (23%)

Spectral data were identified with those of an authentical sample.

(4-carbmethoxyphenyl)methyl-d_2-dibenzylphosphine oxide **2r** (eluted with chloroform) 0.162 g (17%)
m.p. 141–143°C
IR (KBr) ν = 1200 P=O, 1705 C=O, 1295 C(O)OC cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.08 (d, J = 13.92 Hz, PCH_2, 4H), 3.90 (s, $COOCH_3$, 3H), 7.20–7.40 (m, aromat, 12H), 8.00 (d, J = 7.81, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 41.29
Anal. Calcd. for $C_{23}H_{21}D_2O_3P$: C, 72.61; HD, 6.62; found: C, 72.80; HD, 6.31

Run 42

4-bromobenzyl bromide **1h** (eluted with hexane) 0.062 g (10%)
4-bromobenzyl methyl ether **6h** (eluted with hexane:chloroform 4:1) 0.171 g (34%)
IR (Film) ν = 1120 C—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.38 (s, OCH_3, 3H), 4.39 (s, CH_2O, 2H), 7.15–7.25 (m, aromat, 2H), 7.40–7.52 (m, aromat, 2H)
dimethyl (4-bromophenyl)methyl-d_2-phosphonate **2t** (eluted with chloroform) 0.386 g (55%)
m.p. 49–52°C
IR (KBr) ν = 1260 P=O, 1050 P—O—C cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.68 (d, J = 10.91 Hz, $POCH_3$, 6H), 7.10–7.25 (m, aromat, 2H), 7.35–7.50 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 28.56

Run 43

4-methyl-*d*-bromobenzene **3u** (eluted with hexane) 0.052 g (12%)
^{1}HNMR ($CDCl_3$) δ = 2.10 (t, J = 2.23 Hz, CH_2D, 2H), 6.51–6.61 (m, aromat, 2H), 6.86–6.95 (m, aromat, 2H)
Deuterium incorporation minimum value 97%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-bromobenzyl bromide **1h** (eluted with hexane) 0.081 g (13%)
4-bromobenzyl methyl ether **6h** (eluted with hexane:chloroform 4:1) 0.161 g (32%)
methyl dibenzylphosphinate **7** (eluted with chloroform) 0.065 g (10%)

Spectral data were identified with those of an authentical sample.

(4-bromophenyl)methyl-d_2-dibenzylphosphine oxide **2u** (eluted with chloroform) 0.411 g (41%) m.p. 160–162°C
IR (KBr) ν = 1195 P=O cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.04 (d, J = 13.57 Hz, CH_2P, 4H), 7.10–8.00 (m, aromat, 19H)
^{31}PNMR ($CDCl_3$) δ = 40.80
Anal. Calcd. for $C_{21}H_{18}D_2BrOP$: C, 62.85; HD, 5.52; found: C, 63.01; HD, 5.20

Crossover Experiment of the Michaelis-Becker Reaction Between 4-Substituted Benzyl Bromide **1** *and the Sodium Salt of Diisopropyl Phosphite in THF Solution: General Procedure*

To a suspension of NaH (1.5 mmol, 0.036 g) in 5 mL of THF was added diisopropyl phosphite (1.25

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mmol, 0.21 g) in 5 mL of THF. When the evolution of hydrogen had ceased, 4-substituted benzyl bromide **1** (4-nitrobenzyl bromide, 4-cyanobenzyl bromide, 4-(phenylsulfonyl)benzyl bromide) (1.25 mmol) with benzyl bromide (6.25 mmol, 1.07 g) in 2.5 mL of THF were added and the reaction mixture was stirred for 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography. The yields are shown in Table III.

Influence of Light on the Michaelis-Becker Reaction Between 4-Nitrobenzyl Bromide **1a** *and the Sodium Salt of Diisopropyl Phosphite in THF Solution: General Procedure*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF was added diisopropylphosphite (2.5 mmol, 0.42 g) in 10 mL of THF. When the evolution of hydrogen had ceased the solution was cooled to −45°C and 4-nitrobenzyl bromide **1a** (2.5 mmol, 0.54 g) in 5 mL of THF was added and the reaction mixture was stirred for 30 min at −45°C temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography.

The above experiment was repeated: a) in a flask shielded from all light, b) in a flask irradiated by the 500 W bulb.

The yields and conditions for the reactions carried out under normal conditions: day light, in darkness and in the presence of light (500 W bulb) are summarized in Table IV.

Influence of Light on the Michaelis-Becker Reaction Between 4-substituted Benzyl Bromide **1** *and the Sodium Salt of Diisopropyl Phosphite in THF Solution: General Procedure*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF was added diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF. When the evolution of hydrogen had ceased, 4-substituted-benzyl bromide **1** (4-cyanobenzyl bromide, 4-(phenylsulfonyl)benzyl bromide, 4-bromobenzyl bromide, 4-carbethoxybenzyl bromide) (2.5 mmol) in 5 mL of THF was added and the reaction mixture was stirred for 3 hours at room temperature then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuo and the products were separated by radial chromatography.

The above experiment was repeated: a) in a flask shielded from all light, b) in a flask irradiated by the 500 W bulb.

The yields and conditions for the reactions carried out under normal conditions: day light, in darkness and in the presence of light (500 W bulb) are summarized in Table IV.

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